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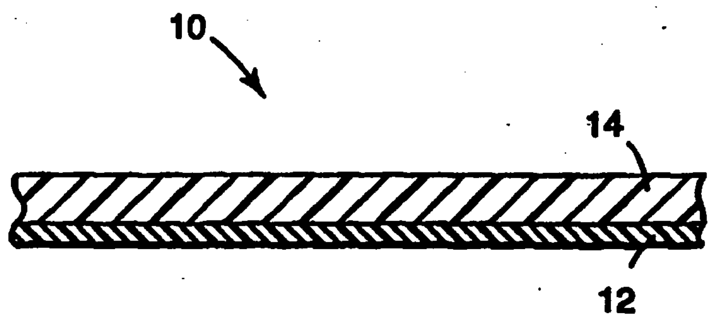
(54) Title: INKJET RECORDING MEDIUM

(57) Abstract

An inkjet recording medium is provided, having a hydrophilic, microporous, polymeric membrane with a hygroscopic layer residing on a major surface thereof. The hygroscopic layer receives an inkjet image and the hydrophilic, microporous, polymeric membrane diffuses the water and other solvents from the ink to provide rapid drying and a precise inkjet image. A method of forming the precise inkjet image is also disclosed using conventional inkjet printers using the disclosed inkjet recording medium. Uses for the inkjet recording medium range from overhead projector transparencies to graphic appliqués such as outdoor billboards. A second embodiment provides a field of pressure sensitive adhesive on at least a portion of the side of the hydrophilic, microporous, polymeric membrane opposite the hygroscopic layer containing the permanent, precise image.



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Inkjet Recording Medium

Field of the Invention

This invention relates to inkjet recording media that rapidly produces precise images.

Background of the Invention

Inkjet recording media are preferred for producing images from computer printers and the like for applications ranging from desktop publishing using paper or overhead transparency stock to commercial graphic displays such billboards and other outdoor advertising media.

Three approaches have generally been taken in the production of inkjet media in the attempt to rapidly produce precise images using both pigment and dye based inks. All three approaches have had unresolved deficiencies and problems.

The most basic approach has been to employ paper as the receptor for inkjet images. Plain paper does not exhibit high image density or accurate dot reproduction because the dye or pigments contained in the solvents used in the inkjet ink diffuse into the pores of the paper. The result is a muted image with low resolution.

An improvement on this approach is to apply a coating on top of the paper which serves to trap the dyes and pigments on the surface. The hydrophilic coating or layer easily receives the inkjet image, and the solvents propelling the dyes and pigments diffuse into the underlying paper. This improves the image appearance because of enhanced color density and resolution. This layer most often comprises a water soluble or swellable layer and can include hydrophilic fillers such as silica. An example of a recent refinement is U.S. Pat. No. 5,213,873.

Although this media provides acceptable image quality, the base exhibits all the inherent weaknesses of paper, such as lack of dimensional stability and water sensitivity. The underlying paper was not durable and was especially susceptible to curling and other deformation in the presence of too much water from the ink or from the environment. Hygroscopic expansion and contraction alone will limit the

use of paper for large, multi-panel graphics because of buckling or shrinkage. Outdoor uses were particularly limited.

A second approach is demonstrated by the use of inkjet imaging on transparent polymeric or durable bases for the generation of transparencies. Many patents disclose the use of an ink receptive layer on transparent, polymeric materials. Examples include U.S. Pat. No. 4,935,307 and U.S. Pat. No. 4,956,230. This layer is often comprised of a water soluble or swellable layer. One of the major problems with these materials is that because the base film does not absorb the water or liquids present in the inkjet ink, all the ink carrier solvent remains in the hydrophilic coating. Enhanced drying times are claimed to be in the four minute range. This results in a surface that remains soft or tacky before finally drying. Further enhancements in clear coatings for visuals are represented in Iqbal, et. al. including U.S. Pat. No. 5,134,198 and U.S. Pat. No. 5,219,928, on interpenetrating networks. When these materials are coated on standard polymeric films, drying times are longer than desired, although faster than standard water soluble materials providing images with good durability.

Other recent work has been directed toward eliminating the smearing and tackiness of hygroscopic coatings on polymeric films. These include various methods to keep the liquids away from the surface to prevent tackiness. These more recently include multiple layers, such as in U.S. Pat. No. 4,379,804, U.S. Pat. No. 5,192,617 and U.S. Pat. No. 5,352,736 whereby the top layer transports the solvent to a lower layer that is hydrophilic. This system works well but requires multiple coating operations. Furthermore, all solvent entering the system must evaporate by exiting the same side that it entered.

Often crosslinking agents may be employed in the hygroscopic coating to prevent excessive water sensitivity. The tradeoff is that any decrease in water absorption results in a loss of capacity of the coating to collect all ink deposited on the surface without dot spread. Various work at balancing these properties is discussed in U.S. Pat. No. 5,241,006, U.S. Pat. No. 5,208,092, U.S. Pat. No. 5,376,727, and U.S. Pat. No. 4,904,519.

The third approach has been to employ a hydrophilic, porous, polymeric substrate or polymer/paper fiber blends (without any other ink receiving coating or layer thereon) for directly receiving the inkjet image. These materials can be dimensionally stable, but do not show good image density and resolution. Image dry times are often very rapid.

The hydrophilic, porous, polymeric substrate easily receives the inkjet image, and the solvents carrying the dyes and pigments diffuse into the substrate. But the diffusion of the solvents also caused a diffusion of the dyes and pigments that prevented the formation of a precise, sharp image. One solution to reduce the diffusion of a precise image and to increase apparent image density was provided in U.S. Pat. No. 5,443,727 which requires the heating of the substrate to collapse the porosity of the substrate and the sealing of the image in its intended position. The heating operation is difficult, particularly with large graphics where shrinkage and wrinkling must be avoided.

Summary of the Invention

The art of producing inkjet recording media has not found the appropriate combination of materials best designed to provide a precise inkjet image that dries rapidly and is particularly suitable for applications requiring dimensional stability. The present invention has recognized the problem resides in providing appropriate layers in inkjet recording media for separating solvents in the inks from the dyes and pigments in the inks without causing undue diffusion of the image.

The present invention solves the problems found in the art by providing a combination of layers in inkjet recording media that produce rapid-drying, precise images.

In one aspect, the present invention provides an inkjet recording medium comprising a hydrophilic, microporous, polymeric membrane having opposing major surfaces and a non-porous hygroscopic layer residing on at least one major surface of the membrane.

The combination of the two layers of the inkjet recording medium provide features that neither layer alone can successfully provide to solve the problems identified in the art.

The hygroscopic layer provides a means for receiving an inkjet image and retaining dyes and pigments contained in the ink.

The hydrophilic, microporous, polymeric membrane provides a means for durably supporting the hygroscopic layer containing the inkjet image and also a means for diffusing the solvents contained in the inks from the dyes and pigments retained in the hygroscopic layer.

The combination of the hygroscopic layer and the hydrophilic, microporous, polymeric membrane provides the means for rapidly producing a precise inkjet image in a durable medium.

For purposes of this invention, "hydrophilic" means that the contact angle of the liquid on the surface is less than 90 degrees.

For purposes of this invention, "hygroscopic" means the layer is capable of being wet by a water-based blend of solvents and surfactants used in inkjet inks, and the water-based blend is absorbed by the layer.

For purposes of this invention, "microporous polymeric membrane" means a polymer film that contains an interconnecting void structure.

For purposes of this invention, "non-porous layer" means a layer that does not contain an interconnecting void structure

For purposes of this invention, "hydrophilic microporous polymeric membrane" means a polymer film whereby the capillary and surface tension forces of the water-based liquids, such as a blend of solvents and surfactants, will cause the liquid to be absorbed, i.e., to enter the pores of the membrane. Preferably, the membrane will absorb water with less than one atmosphere of pressure.

For the purposes of this invention, "precise" means that dot spread resulting from applying an ink jet drop to the sheet is below a level at which the resolution of the image is adversely affected. Examples without precise imaging might show image bleed, uneven edges, or mottled colors.

In another aspect, the present invention provides an inkjet recording medium just described but also including a layer of pressure sensitive adhesive applied to at least a portion of the second surface of the membrane.

In another aspect, the present invention provides an inkjet recording medium just described but also including an inkjet image permanently located in the hygroscopic layer.

In another aspect, the present invention provides a method of forming a rapid-drying, precise inkjet image, comprising the steps of providing an inkjet recording medium comprising a hydrophilic, microporous, polymeric membrane having opposing sides and a hygroscopic non-porous layer on at least one side of the membrane; introducing inkjet ink to the medium in the pattern of a desired image.

One feature of the invention is that the inkjet recording medium rapidly provides a precise inkjet image on a durable polymeric substrate.

Another feature of the invention is that the inkjet recording medium rapidly provides the precise, high density inkjet image without the requirement of special post-treatment of the medium.

An advantage of the invention is that the inkjet recording medium is produced from a combination of two layers of known and commercially available materials without complicated manufacturing or storage requirements.

Another advantage of the present invention is that the medium does not require the presence of particles such as corn starch, silica, or clay, in either layer of the medium to provide better imaging or handleability. However, those materials may provide additional handling benefits.

Other advantages of the invention are that the inkjet recording medium provides a better reflective color density, better dot sharpness, dimensional stability, and quicker drying times than found in conventional inkjet recording media.

The embodiments of the invention are described with reference to the following drawings.

Brief Description of the Drawing

FIG. 1 is a cross-sectional view of one embodiment of the invention.

FIG. 2 is a cross-sectional view of a second embodiment of the invention.

FIG. 3 is a photomicrograph of a cross-section of a hydrophilic, microporous, polymeric membrane of the prior art.

FIG. 4 is a photomicrograph of the cross-section of an embodiment of the invention of a hydrophilic, microporous, polymeric membrane having opposing sides and a hygroscopic layer residing on at least one side of the membrane.

FIG. 5 is a photograph of a hydrophilic, microporous, polymeric membrane of the prior art.

FIG. 6 is a photograph of an embodiment of the invention of a hydrophilic, microporous, polymeric membrane having opposing sides and a hygroscopic layer residing on at least one side of the membrane.

Embodiments of the Invention

FIG. 1 illustrates one embodiment of the invention. Inkjet recording medium 10 is comprised of a hydrophilic, microporous, polymeric membrane 12 having a hygroscopic layer 14 thereon. The layer 14 can be coated on or laminated to the membrane 12 using techniques known to those skilled in the art of coating or laminating of multiple layered constructions. Nonlimiting examples of coating or laminating techniques include notched bar coating, curtain coating, roll coating, extrusion coating, gravure coating, calendering, and the like.

Hydrophilic, microporous, polymeric membrane 12 is hydrophilic and receptive of aqueous solvents typically used in inkjet formulations. Microporous membranes are available with a variety of, pore sizes, compositions, thicknesses, and void volumes. Microporous membranes suitable for this invention preferably have adequate void volume to fully absorb the inkjet ink discharged onto the hydrophilic layer of the inkjet recording medium. It should be noted that this void volume must be accessible to the inkjet ink. In other words, a microporous membrane without channels connecting the voided areas to the hygroscopic surface

coating and to each other (i.e., a closed cell film) will not provide the advantages of this invention and will instead function similarly to a film having no voids at all.

Void volume is defined in ASTM D792 as the (1-Bulk density/Polymer density)*100. If the density of the polymer is not known, the void volume can be determined by saturating the membrane with a liquid of known density and comparing the weight of the saturated membrane with the weight of the membrane prior to saturation. Typical void volumes for hydrophilic, microporous, polymeric membrane 12 range from 10 to 99 percent, with common ranges being 20 to 90%.

Void volume combined with membrane thickness determines the ink volume capacity of the membrane. Membrane thickness also affects the flexibility, durability, and dimensional stability of the membrane. Membrane 12 can have a thickness ranging from about 0.01 mm to about 0.6 mm (0.5 mil to about 30 mils) or more for typical uses. Preferably, the thicknesses are from about .04mm to about .25mm (about 2 mils to about 10 mils).

The liquid volume of typical inkjet printers is approximately 40 to 140 picoliters per drop. Typical resolution is 118 to 283 drops per centimeter. High resolution printers supply smaller dot volumes. Actual results indicate a deposited volume of 1.95 to 2.23 microliters per square centimeter with each color. Solid coverage in multicolor systems could lead to as high as 300% coverage (using undercolor removal) thus leading to volume deposition of 5.85 to 6.69 microliters per square centimeter.

Hydrophilic, microporous, polymeric membrane 12 has a pore size that is less than the nominal drop size of the inkjet printer in which the inkjet recording medium is to be used. The pore size may be from 0.01 to 10 micrometers with a preferred range of from 0.5 to 5 micrometers with pores on at least one side of the sheet.

The porosity, or voided aspect, of membrane 12 need not go through the entire thickness of the membrane, but only to a sufficient depth to create the necessary void volume. Therefore, the membrane may be asymmetric in nature, such that one side possesses the aforementioned properties, and the other side may be more or less porous or non-porous. In such a case, the porous side must have

adequate void volume to absorb the liquid in the ink that is passed through the hygroscopic layer 14.

Nonlimiting examples of hydrophilic, microporous, polymeric membranes include polyolefins, polyesters, polyvinyl halides, and acrylics with a micro-voided structure. Preferred among these candidates are a microporous membrane commercially available as "Teslin" from PPG Industries as defined in U.S. Pat. No. 4,833,172 and hydrophilic microporous membranes typically used for microfiltration, printing or liquid barrier films as described in U.S. Pat. Nos. 4,867,881, 4,613,441, 5,238,618, and 5,443,727. Teslin microporous membrane has an overall thickness of approximately 0.18 mm, and the void volume has been measured experimentally to be 65.9%. The ink volume capacity of the membrane is thus 11.7 microliters per square centimeter. Therefore, this membrane has sufficient void volume combined with thickness to fully absorb the ink deposited by most inkjet printers, even at 300% coverage, without considering the amount retained in the hygroscopic layer.

Membrane 12 can optionally also include a variety of additives known to those skilled in the art Nonlimiting examples include fillers such as silica, talc, calcium carbonate, titanium dioxide, or other polymer inclusions. It can further include modifiers to improve coating characteristics, surface tension, surface finish, and hardness.

Hygroscopic layer 14 can be a coated layer or laminated layer on that portion of membrane 12 upon which the inkjet image is to be formed. Thus, layer 14 need not cover completely the membrane 12. Nor need layer 14 cover both sides of membrane 12. Layer 14 preferably lies substantially on the surface of membrane 12 and does not contact the inner pore surfaces of the membrane. Depending on the ultimate purpose for the medium 10, at least one side of membrane 12 may be covered at least in part by layer 14 and the other side may be sealed or coated with another material, such as an anti-static coating, adhesive, barrier layer, light blocking layer, strength enhancing layer, etc.

Layer 14 can be constructed from a variety of naturally occurring or synthetically constructed materials known to those skilled in the art for providing an

ink receptive surface. Nonlimiting examples of the materials used for forming layer 14 include polyvinyl alcohol, polyvinyl pyrrolidone, cellulose derivatives such as carboxymethyl cellulose, polyethylene oxide, water soluble starches and gums, . In addition, inorganic fillers such as silica, talc, calcium carbonate, titanium dioxide can be beneficial to enhance handling, opacity, strength, wetting, or control viscosity. Mordants, such as in U.S. Pat. No. 5354813 and 5403955 and color stabilizers can also be included.

Of these materials, hygroscopic, polymeric coatings are preferred due to ease of manufacturing and performance to provide an ink receptive surface for receiving and permanently contacting and retaining dyes and pigments in a precise inkjet image. Of these coatings, poly(N-vinyl lactams), polyethylene oxides, methyl and propyl cellulose derivatives, and poly(vinyl alcohols) are particularly preferred.

Hygroscopic layer 14 may be formed on membrane 12 using a number of techniques, including coating, laminating, or co-extrusion. When a hydrophilic coating solution is applied to the membrane, solution viscosity and concentration will affect the performance of the resulting inkjet recording medium. For example, low viscosity coating solutions coated on membranes with very high porosity and/or large pore size tend to fill the pores, resulting in a coated membrane that is saturated with hygroscopic polymer and has little or no coating on the surface. Membranes coated in such a manner do not meet the requirements of this invention because the imaged medium usually exhibits lower image density and contrast and can dry more slowly. Techniques for achieving deposition of the hygroscopic layer 14 on the membrane 12 are demonstrated in the examples.

Solution viscosity of coating solutions is controlled by a variety of factors including coating solvent, polymer solubility, polymer molecular weight, temperature, etc. For the sake of this invention, low viscosity solutions are considered solutions with intrinsic viscosity of less that 100,000 centipoise when measured with an instrument such as a Brookfield viscometer.

Layer 14 can have a thickness ranging from about 2 micrometers to 35 micrometers. Preferably, the thicknesses are from about 3 micrometers to 15 micron. Greater thicknesses tend toward the problem of surface tackiness and curl.

The combination of membrane 12 and layer 14 is capable of providing a precise image with rapid drying, with drying times typically within about 15 to 30 seconds after printing.

Both membrane 12 and layer 14 can include a variety of additives that further enhance the inkjet recording medium of the present invention.

Layer 14 can itself comprise multiple layers with the outermost layer containing scratch resistant compositions such as silica filled acrylic polymers, moisture or fingerprint resistant compositions such as particulate fillers, ultraviolet light absorbing compositions such as benzophenones, and handling aids such as silicone or wax block and mar aids. Therefore, the hygroscopic layer 14 can contain mordants, ultraviolet light absorbers, anti-oxidants, fillers, mar aids, blocking aids, or other materials to improve the image stability or handling.

Optionally, medium 10 can have a backside layer coating the opposing major surface of membrane 12 to reduce or minimize curling of medium 10 after imaging has occurred. Nonlimiting examples of backside layer materials include materials with hygroscopic expansion rates similar to layer 14. Such materials would include starches, gums, and other water swellable polymers.

Further, optionally, medium 10 can have the opposing major surface of membrane 12 sealed due to a saturation coating or a differential manufacturing process. Nonlimiting examples of such processes are pressure sensitive adhesive coating, calendering, hot roll casting, co-extrusion, lamination, and the like.

Further, optionally, medium 10 after imaging can have the pore structure of membrane 12 collapsed to provide transparency by a post treatment such as heating or calendering, such as disclosed in U.S. Pat. No.5,443,272.

FIG. 2 illustrates a second embodiment of the invention. Inkjet recording medium 20 is comprised of a hydrophilic, microporous, polymeric membrane 22 having a hygroscopic layer 24 thereon. Membrane 22 and layer 24 correspond to membrane 12 and layer 14 of the embodiment of FIG. 1., respectively. Medium 20 further comprises a layer 26 of pressure sensitive adhesive that covers at least a portion of the side of membrane 22 opposite layer 24. During storage, a release liner 28 covers layer 26 until the medium is ready for use.

Pressure sensitive adhesives useful for layer 26 can be any conventional pressure sensitive adhesive that adheres to both membrane 22 and to the surface of the item upon which the inkjet recording medium having the permanent, precise image is destined to be placed. Pressure sensitive adhesives are generally described in Satas, Ed., Handbook of Pressure Sensitive Adhesives 2nd Ed. (Von Nostrand Reinhold 1989). Pressure sensitive adhesives are commercially available from a number of sources. Particularly preferred are acrylate pressure sensitive adhesives commercially available from Minnesota Mining and Manufacturing Company of St. Paul, Minnesota and generally described in U.S. Pat. Nos. 5,141,790, 4,605,592, 5,045,386, and 5,229,207.

Release liners for liner 28 are also well known and commercially available from a number of sources. Nonlimiting examples of release liners include silicone coated kraft paper, silicone coated polyethylene coated paper, silicone coated or non-coated polymeric materials such as polyethylene or polypropylene, as well as the aforementioned base materials coated with polymeric release agents such as silicone urea, urethanes, and long chain alkyl acrylates, such as defined in U.S. Pat. No. 3,957,724; 4,567,073; 4,313,988; 3,997,702; 4,614,667; 5,202,190; and 5,290,615.

Usefulness of the Invention

Inkjet recording media of the present invention can be employed in any environment where inkjet images are desired to be precise, stable, and rapid drying. Commercial graphic applications include opaque signs and banners.

Inkjet recording media of the present invention have dimensional stability as measured by hygroscopic expansion of less than 1.5% size change in all directions with a relative humidity change from 10% relative humidity to 90% relative humidity. As such, the media of the present invention is preferred over coated papers because the paper is apt to change shape or dimension during processing or during use.

Inkjet recording media of the present invention can accept a variety of inkjet ink formulations to produce rapid drying and precise inkjet images. The thickness and composition of the individual layers of the inkjet recording medium can be varied for optimum results, depending on several factors, such as: ink droplet volume; ink liquid carrier composition; ink type (dye, pigment, or blend); and manufacturing technique (machine speed, resolution, roller configuration); etc. Commonly, inkjet ink formulations have a combinations of colored dyes and/or pigments in water blended with other solvents. Both water and the other solvents carry the dyes and pigments into layer 14 or 24 and then continue into membrane 12 or 22 for rapid drying of the image in the layer 14 or 24 to form the precise image.

Drying can be measured as the time required before the image becomes tack free or does not smear when lightly rubbed.

The formation of precise inkjet images is provided by a variety of commercially available printing techniques. Nonlimiting examples include thermal inkjet printers such as DeskJet brand, PaintJet brand, Deskwriter brand, DesignJet brand, and other printers commercially available from Hewlett Packard Corporation of Palo Alto, California. Also included are piezo type inkjet printers such as those from Seiko-Epson, spray jet printers and continuous inkjet printers. Any of these commercially available printing techniques introduce the ink in a jet spray of a specific image into the medium of the present invention. Drying is much more rapid under the present invention than if the hygroscopic top coating or coatings were to be applied to a similar non-porous media.

FIG. 3 and FIG. 4 demonstrate a comparison of the medium 10 of the present invention comprising membrane 12 and layer 14 and a microporous membrane 12 alone. FIG. 3 is a photomicrograph cross-sectional view of a microporous membrane 12 at about 5,000 magnification. FIG. 4 is a photomicrograph cross-sectional view at the same magnification of medium 10 having a membrane 12 with a major surface, upon which hygroscopic layer 14 resides. As seen in FIG. 4, essentially none of the hygroscopic layer 14 resides within the porous surfaces of membrane 12.

The benefit of the construction of medium 10 can be easily seen by a comparison of FIGS. 5 and 6. FIG. 5 is a photograph of about 40 magnification of the membrane 12 of FIG. 3 upon which an image of a distinct pattern resides. The image was placed on the membrane by a Deskwriter C brand printer using Hewlett Packard brand inkjet inks. FIG. 6 is a photograph of the same magnification of the medium of FIG. 4 upon which the same image of that distinct pattern resides. The image was placed on the membrane by a Deskwriter C brand printer using Hewlett Packard brand inkjet inks . FIG. 6 shows a far more precise image created by the combination of membrane 12 and layer 14 to form medium 10.

A comparison of the photographs of FIGS. 5 and 6 shows how inkjet media of the present invention have better dot sharpness to provide a precise image.

Further as seen in FIGS. 5 and 6, media of the present invention have a better reflective color density which can be measured by reflective optical density.

Media of the present invention can have the same properties of void volume and pore size as that found in the commercially available membranes used to form such media. As seen in FIG. 4, hygroscopic layer 14 essentially resides on a major surface of membrane 12 without essentially altering the effective void volume or pore size of membrane 12 (even though it possible for some voids to become impregnated with hygroscopic layer 14).

Uses of imaged media of the present invention include graphic appliqués, such as for interior decoration or outdoor billboards, trailer trucks, sign faces, mural photographs, and the like.

The following examples provide further explanation of the embodiments of the invention.

Test Methods

Dry time testing:

1) Image the material using an appropriate inkjet printer.

2) Measure the time required such that a light touch with a finger does not smear the ink, damage the image, or reveal excessive image tackiness.

Density Measurements:

All density measurements are reflected optical density and measured with a densitomer using the color filter that gives maximum difference between the image and white.

Examples

Properties of interest on imaged inkjet recording media consist of reflected optical density, dry time, resolution or dot spread, among others. Reflected optical density is measured using techniques well known to those in the printing industry. Examples herein were evaluated with a Gretag SPM50 densitometer from Gretag Limited, CH-8105 Regensdorf, Switzerland. Other instruments will give similar comparisons, but not necessarily the same values. Dry times were measured subjectively by imaging a solid area and determining the length of time until the image did not smudge or smear when rubbed lightly. Dot spread is determined by measuring a single dot line. The lower the number is, the lower is the dot spread. Zero dot spread allows the most accurate reproduction, however, some dot spread will occur because of the spherical drop striking a flat plane and wetting the surface. On coatings that do not dry quickly, dot spread can be observed as the liquid diffuses inside the coating.

Example 1

The following coating solution was prepared:

25.0g PVP-K90 polyvinyl pyrrolidone from ISP (International Specialty Products, 1361 Alps Road, Wayner, NJ 07470)

250.0g De-Ionized Water

The above ingredients were mixed until a clear solution was formed.

A piece of Teslin™ microporous membrane (PPG Industries, One PPG Place, Pittsburgh, PA 15272 USA) with an experimentally determined average pore size of .35 micrometer and a Gurley porosity of 550 seconds per 50 cubic centimeters of air was coated and dried at 70°C to yield a hygroscopic layer having a dry coating weight of 4.2 grams/square meter. The sample was imaged using a Hewlett Packard Deskwriter C brand ink jet printer. This printer delivers approximately 140 picoliters of ink per drop. A scanning electron microscope photograph of a cross section of the above coating indicated that the polymer was predominantly on the surface of the sheet.

Example 1b

For the purposes of comparison, a piece of unmodified Teslin™ microporous membrane was printed in the same manner and designated Example 1b. Table 1 represents the density and dry times for these samples.

Example 2

A sample using the solution of Example 1 was coated as in Example 1 to yield a dry coating weight of 6.6 grams/square meter. The sample was imaged as in Example 1 to determine the effect of higher coating weight. Likewise, the density data is in Table 1. A scanning electron microscope photograph of a cross section of the above coating indicated that the polymer was predominantly on the surface of the sheet.

Example 3

The solution from Example 1 was coated on a microporous membrane as defined in US 5,443,727, Example #5, which is .089 millimeters thick, has a Gurley porosity of 6 seconds per 50 cubic centimeters, and a void volume of approximately 80%. The coating is noted to penetrate and saturate the membrane. The membrane was imaged as above. A scanning electron microscope photograph of a cross section of the above coating indicated that the polymer was present throughout the sheet.

Example 3b

A sample of film from Example 3 prior to coating was imaged for reference.

Example 4

This sample was printed for comparative purposes and represents commercially available materials. 3M Color Transparency Material for Inkjet printers was imaged with the same pattern as in the previous examples. The density on this material represents the maximum achievable density since all material is on the surface and none is lost inside the media. Dry times are excessively long because all liquids must evaporate from the surface of the material.

Table 1

Example	Dry Time (sec)	ROD Black	ROD Cyan	ROD Yellow	ROD Magenta	Black Line Width[1]	Cyan Line Width
1	15	1.74	1.47	1.02	.95	.41/.41	.35/.33
1b	15	.96	.86	.54	.74	.44/.43	.37/.35
2	60	2.08	1.52	1.10	1.00	.45/.45	.38/.38
3	15	1.10	.73	.61	.62	.41/.40	.37/.35
3b	15	.73	.66	.46	.48	.51/.50	.41/.40
4	>300	1.85	1.27	.77	.70	.45/.45	.41/.40

Example 5

The following coating solution was prepared:

50.0g Polyox N-3000 polyethylene oxide from Union Carbide, 39 Old Ridgebury Road, Danbury, CT 06817

950.0g De-Ionized Water

The above ingredients were mixed until a clear solution was formed.

[1] Horizontal/Vertical millimeters width

A piece of cast polypropylene film was coated and dried at 70°C to yield a dry coating weight of 4.2 grams/square meter. The film was then heat laminated to the microporous membrane used in Example 3b through a heat roll laminator operating at 95°C. After the composite was allowed to cool, the polypropylene was stripped off leaving the coating of polyethylene oxide on the microporous membrane. Examination revealed that the coating was on top of the microporous membrane. The coated membrane was imaged as above. The imaging characteristics of polymer are not as good as those of polyvinyl pyrrolidone, but the composite has better image density than uncoated material, thus concluding that lamination is a method which can be used to deposit the hygroscopic top coating above the microporous film where coating the material results in complete saturation of the film.

Example 5b is a control printing of uncoated material.

Example 6

The following solution was prepared:

25.0g Polyox N-3000 Brand Polyethylene Oxide from Union Carbide

25.0g PVP-K90 polyvinyl pyrrolidone from

950.0g De-Ionized Water

1000.0g Isopropanol

The above ingredients were mixed until a clear solution was formed.

The above solution was coated on a cast polypropylene film and dried in a oven operating at 77°Celcius (170°Farenheit) to yield a dry coating thickness of 50 micrometers corresponding to a coating weight of 5g/sq meter.

The coated material was laminated to a Teslin™ microporous membrane using a pressure of approximately 2.8 kilograms/sq. cm(40 pounds per sq.

inch) at 96°C (205°F for 3.8 seconds in a heated roll laminator with one heated steel roll and one unheated rubber roll. The material was imaged as previously described.

Table 2

Example	Dry Time (sec)	ROD Black	ROD Cyan	ROD Yellow	ROD Magenta	Black Line Width	Cyan Line Width
5	120	.97	1.33	.86	.90	.48/.42	.43/.38
5b	15	.75	.76	.51	.48	.54/na	.44/na
6	15	1.27	1.13	.78	.64	.41/.43	.38/.41
6b	15	.89	.83	.48	.58	.53/.47	.43/.46

In the following examples, Teslin™ microporous membrane was coated on one side with a pressure sensitive adhesive (75 micrometers thick) with a release liner (75 micrometers thick) was used.

Test patterns were printed with 100% color blocks of cyan, magenta, yellow, black (one color-black), red, green and blue on a Hewlett Packard DesignJet™ 650C fitted with HPS1640 cartridges available for the Hewlett-Packard Desk3et 1200C.

Reflection densities were measured using a Gretag SPM-50 (settings 2', D65, ANSI T, Abs, No).

Example 7

The following is intended to exemplify the quick drying properties of the Teslin™ membrane but also the disadvantages of low density images.

A piece of the uncoated Teslin™ membrane was loaded into the DesignJet™ 650C equipped as above, and the test pattern printed. All colors felt dry to the touch

immediately after printing by touching with the pads of the fingers to detect any residual tack or removal of color off the image onto the fingers.

Densities of the were measured. Densities are shown in Table 3 and are overall lower than those of the coated samples.

Example 8

A 10% solution by weight (weight/weight solution) of polyvinylpyrrolidone PVP K15 available from ISP (International Specialty Products, 1361 Alps Road, Wayne, NJ 07470) was made in ethanol.

A sample of the Teslin™ was coated with the above solution using a notch bar (knife coater) using a gap setting of 3 mil to produce an inkjet recording medium.

A piece of the PVP K15-coated Teslin™ was loaded into the DesignJet™ 650C equipped as above, and the test pattern printed. All colors felt dry to the touch immediately after printing by touching with the pads of the fingers to detect any residual tack or removal of color off the image onto the fingers. Visually the image looked denser than that of a plain Teslin™ membrane of Example 7.

Densities of the colors were measured. Densities are shown in Table 3 and are overall higher than those of the uncoated samples.

Example 9

This example is intended to illustrate that density obtained depends on coating solution concentration as well as the coating formulation.

A 30% solution by weight (weight/weight solution) of polyvinylpyrrolidone PVP K15 available from ISP (International Specialty Products, 1361 Alps Road, Wayne NJ 07470) was made in ethanol.

A sample of the Teslin™ membrane was coated with the above solution using a notch bar (Knife coater) using a gap setting of 3 mil to produce an inkjet recording medium.

A piece of the resulting inkjet recording medium was loaded into the DesignJet™ 650C equipped as above, and the test pattern printed. All colors felt dry to the touch immediately after printing by touching with the pads of the fingers to detect any residual tack or removal of color off the image onto the fingers. Visually the image looked denser than that on the plain Teslin™ membrane in Example 7 and also denser than the inkjet recording medium of Example 8. Densities of the colors were measured. Densities are shown in Table 3.

Example 10

This is intended to demonstrate another type of solution that can be used to coat the Teslin™ (or other microporous films) for improvements in density over the plain film while maintaining the excellent drying characteristics necessary for quick handling after printing and for quick drying with future generations of printers with perhaps wide format arrays or other quick ink jet printing means.

A solution/dispersion was made up as follows:

Ten grams of PVP K15 polyvinyl pyrrolidone available from ISP (International Specialty Products, 1361 Alps Road, Wayne, NJ 07470) was made in ethanol. The solution was vigorously stirred and 10g of Aerosil 380 silica added (available from Degussa Corporation, Silica Division, 425 Metro Place North, Suite 450, Dublin, Ohio 43017). The mixture was homogenized for five minutes on one third speed using a homogenizer fitted with the disintegrator screen (available from Silverson Machines, Inc., P O Box 589, East Longmeadow, MA 01028).

A sample of the Teslin™ membrane was coated with the above mixture using a notch bar knife coater) using a gap setting of 3 mil to produce an inkjet recording medium.

A piece of the above medium was loaded into the DesignJet™ 650C equipped as above, and the test pattern printed. All colors felt dry to the touch immediately after printing by touching with the pads of the fingers to detect any residual tack or removal of color off the image onto the fingers. Visually the image looked denser than that on any of the samples in Examples 7 through 9. Densities of the colors were measured. Densities are shown in Table 3 and are overall higher than those of the other samples.

Example 11

The 30% solution of the PVP K15 described in Example 9 was coated onto plain 4 mil polyester (polyethylene terephthalate) film using a notch bar set at a 3 mil gap.

A piece of the PVP K15-coated polyester was loaded into the DesignJet™ 650C equipped as above, and the test pattern printed. All colors were wet to the touch immediately after printing by touching with the pads of the fingers. Color smeared off onto the fingers easily. The image could easily be smeared and felt tacky ten minutes after printing had finished, and even twenty minutes after printing the image felt tacky and could be smeared.

All coatings described in these examples were dried at 110°C (230°F) for three minutes.

Table 3

Material	ROD Cyan	ROD Magenta	ROD Yellow	ROD Black	Dry Time
Example 7 (Plain Teslin)	0.89	0.667	0.5	0.703	immediate
Example 8 (Teslin+10% PVPK15)	0.896	0.705	0.612	0.646	immediate
Example 9 (Teslin+30% PVPK15)	0.79	0.613	0.66	0.62	immediate
Example 10 (Teslin+PVPK15/ Aerosil380)	1.484	1.194	0.913	1.005	immediate
Example 11 (PET base)					>20 min.

The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. An inkjet recording medium comprising a hydrophilic, microporous, polymeric membrane having opposing major surfaces and a hygroscopic layer residing on at least one surface of the membrane.

2. The medium of Claim 1 wherein the membrane is a polymer film that absorbs water-based liquids.

3. The medium of Claim 1 whereby the membrane will absorb water with less than one atmosphere of pressure.

4. The medium of Claim 1 whereby the major surface of the membrane opposite the hydrophilic layer is sealed due to a coating or a differential manufacturing process.

5. The medium of Claim 1 whereby the pore structure of Claim 1 is collapsed to provided transparency by a post treatment after imaging such as heating or calendering.

6. The medium of Claim 1 whereby the hygroscopic layer is a water soluble or water swellable coating.

7. The medium of Claim 1 whereby the membrane is selected from the group consisting of polyolefins, polyesters, polyvinyl halides, and acrylics with a micro-voided structure.

8. The medium of Claim 1 whereby the hygroscopic layer contains mordants, ultraviolet light absorbers, anti-oxidants, fillers, mar aids, blocking aids, or other materials to improve the image stability or handling.

9. The medium of Claim 1 wherein the major surface of the membrane opposite the hygroscopic layer is coated with an adhesive that allows subsequent bonding to another surface.

10. An inkjet image, comprising an inkjet recording medium comprising a hydrophilic, microporous, polymeric membrane having opposing major surfaces, a hygroscopic layer residing on at least one surface of the membrane, and an inkjet image permanently contacting the hygroscopic layer.

11. The image according to Claim 10, wherein the image is an overhead transparency image.

12. The image according to Claim 10, wherein the image is a graphic appliqué.

13. The image according to Claim 10, the major surface of the membrane opposite the hygroscopic layer is coated with an adhesive that allows subsequent bonding to another surface.

14. A method of forming a permanent, precise inkjet image, comprising the steps of:

(a) providing an inkjet recording medium comprising a hygroscopic, microporous, polymeric membrane having opposing major surfaces and a hydrophilic layer residing on at least one surface of the membrane; and

(b) introducing inkjet ink into contact with the medium in the pattern of a desired image.

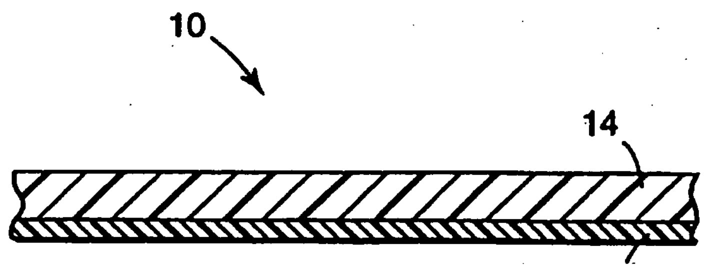

FIG.1

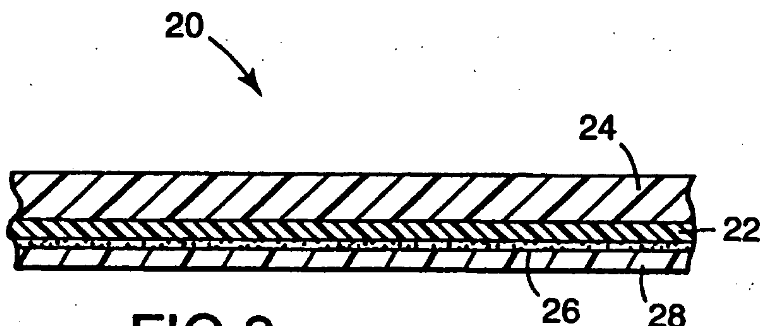

FIG.2

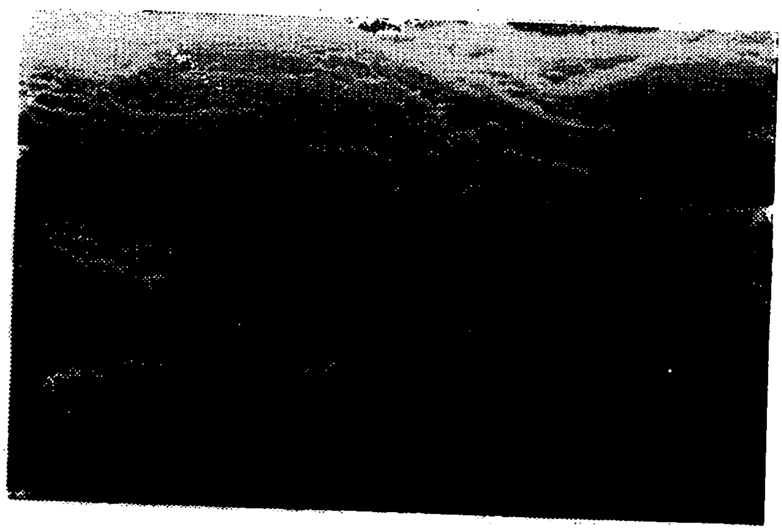

FIG.3
Prior Art

FIG.4

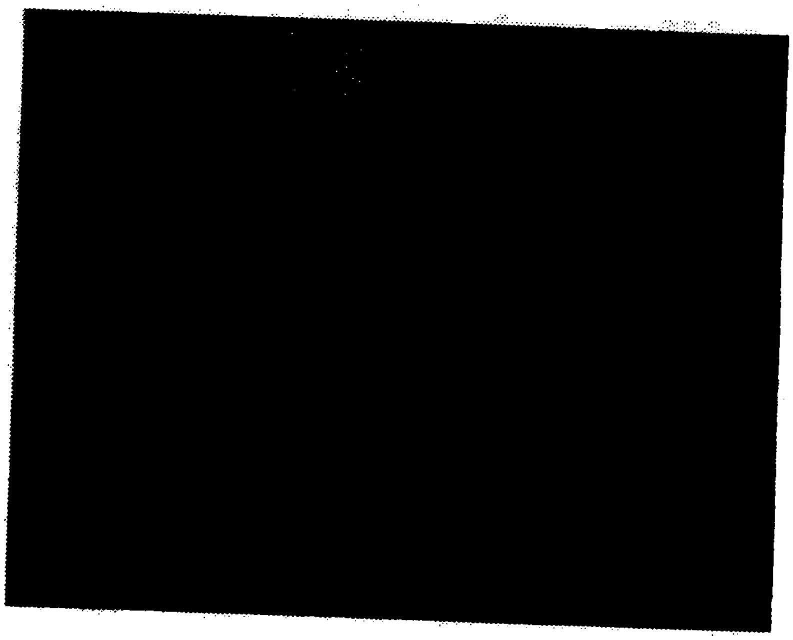

FIG.5
Prior Art

FIG.6

INTERNATIONAL SEARCH REPORT

Inten. nal Application No
PCT/US 97/01730

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M5/00 B41M7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 361 (C-1080), 8 July 1993 & JP 05 051470 A (TORAY IND INC), 2 March 1993, see abstract ---	1-14
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 191 (M-495), 4 July 1986 & JP 61 035276 A (CANON INC), 19 February 1986, see abstract ---	1-14
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 191 (M-495), 4 July 1986 & JP 61 035277 A (CANON INC), 19 February 1986, see abstract ---	1-14

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
22 April 1997	04.06.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Markham, R

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 191 (M-495), 4 July 1986 & JP 61 035278 A (CANON INC), 19 February 1986, see abstract ---	1-14
A	US 5 443 727 A (GAGNON DAVID R) 22 August 1995 cited in the application see column 27, line 59 - column 32, line 46 see examples 32,33,38 ---	5
A	EP 0 673 779 A (MITSUBISHI PAPER MILLS LTD) 27 September 1995 see page 2, line 56 - page 3, line 11 -----	13

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Information on patent family members

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